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(54) **Recording medium and recording method by use thereof.**

(57) A recording medium is provided which comprises having an ink receiving layer containing a polymer complex of a basic polymer and an acidic polymer. A recording method is also provided which performs recording by forming liquid droplets of a recording liquid and permitting the liquid droplets to attach on the surface of a recording medium, wherein the recording liquid is an aqueous ink and the surface of the recording medium contains a polymer complex of a basic polymer and an acidic polymer.

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Recording Medium and Recording Method by Use Thereof

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a recording medium to be used preferably for ink jet recording method, particularly to a recording medium excellent in ink receptivity and giving sharpness and water resistance of the recorded image.

Description of the Related Art

Ink jet recording method performs recording by generating small droplets of ink according to various ink - (recording liquid) discharging systems, such as an electrostatic attraction system, a system of giving mechanical vibration or displacement to ink by use of a piezoelectric element, a system utilizing pressure of bubbles formed by heating ink and permitting ink droplets to fly and attach a part or whole thereof onto a recording medium such as paper. This method is now attracting attention as a recording method which generates less noise and is capable of performing high speed printing and multi-color printing.

For ink jet recording, inks have been used which is composed mainly of water in view of safety and recording characteristics. In most cases, a polyhydric alcohol is added to inks for the purpose of prevention of clogging of nozzles and improvement of discharging stability.

As recording media to be used for the ink jet recording method, there have been employed recording media comprising a porous ink receiving layer provided on an ordinary paper or a substrate called as the ink jet recording paper.

However, as the ink jet recording is improved in performance such as speed-up or multicoloring of recording and is widely spread, higher and broader characteristics are demanded also for the recording medium.

More specifically, the recording medium for ink jet recording for obtaining recorded images of high resolution and high quality needs to satisfy various basic requirements as follows:

(1) reception of ink onto the recording medium should be as rapid as possible;

(2) even when ink dots may be overlapped with each other, the ink attached later should not flow into the dot attached earier;

(3) ink droplets should not diffuse on the recording medium and not become larger in ink dot diameter than is necessary;

(4) the shape of an ink dot should be approximate to a true circle and its circumference should be smooth;

(5) OD (optical density) of an ink dot should be high, without obscurity around the dot; etc.

Further, for obtaining a recorded image quality of high resolution comparable to color photography by the multi-color ink jet recording method, the following performances are further required in addition to the above requisite performances:

(6) the colorants of ink should be excellent in color forming property;

(7) ink fixing characteristic should be excellent since liquid droplets of the same number as that of ink colors may possibly attached on the same spot to overlap each other;

(8) the surface should have gloss;

(9) the degree of whiteness should be high.

Further, while the recorded images obtained by the ink jet recording method have been employed in the past exclusively for surface image observation, recording media suited for uses other than for surface image observation are demanded more with improvement in performances or wide spreading of the ink jet recording device.

Uses of the recording medium other than for surface image observation may include those in which recorded images are projected onto a screen, etc. by means of an optical instrument such as a slide or an OHP (overhead projector), etc. and those in which images are observed by means of color resolution plates during preparation of a positive plate for color printing, and a CMF (a color mosaic filter), etc. to be used for color display such as liquid crystal, etc.

The transmitted light through the recorded images becomes a problem in the recording medium in these uses, which is different from the uses for surface image observation where diffused light mainly from a recorded image is observed. Accordingly, light transmissivity, particularly excellent linear transmittance is required in addition to the requisite performances in general of the recording medium for ink jet recording.

Prior to the present invention, however, no recording medium has not been known which satisfies all of these requisite performances.

Most of the recording media for surface image observation of the prior art have employed a system in which a porous ink receiving layer is provided on the surface and the recording agent is fixed by reception of the ink into the porous voids, and hence the surface of the recording medium lacks gloss due to the porous structure.

On the other hand, in the surface of non-porous ink receiving layer, a non-volatile component such as polyhydric alcohol, etc. in the ink will remain even after recording on the surface of the recording medium for a long time, whereby drying for fixing ink is prolonged, this involving the drawbacks such that clothings may be soiled by contact with the recorded images or that the recorded images may be damaged.

Further, in the case of a recording medium employing a water-soluble polymer for formation of an ink receiving layer in order to enhance the affinity and receptivity for ink, the surface of the ink receiving layer becomes sticky under highly humid conditions, whereby the problems arises such that it is adhered onto the delivery roller when mounted on a printer, thus failing to be conveyed, and also that the recording medium will be subject to blocking when placed one upon another.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a recording medium for use in ink jet recording which is particularly excellent in ink receptivity and giving water resistance and sharpness of recorded image.

Another object of the present invention is to provide a recording medium for use in full color ink jet recording which is excellent in ink receptivity, and giving sharpness of recorded image and surface gloss, and also free from stickiness of the surface, blocking, etc. even under highly humid conditions.

Still another object of the present invention is to provide a recording medium for use in ink jet recording, which can be used for observation by projection of recorded image by means of an optical instrument such as a slide or an OHP, or which can be used for observation of transmitted light such as a color resolution plate during preparation of a positive plate for color printing or a CMF, etc. to be used for color display such as liquid crystal.

The above and other objects of the present invention can be accomplished by the present invention as described below.

According to the present invention, there is provided a recording medium which comprises having an ink receiving layer containing a polymer complex of a basic polymer and an acidic polymer.

In another aspect of the present invention, there is also provided a recording method which performs recording by forming liquid droplets of a recording liquid and permitting the liquid droplets to be attached on the surface of a recording medium, wherein the recording liquid is an aqueous ink and the surface of the recording medium contains a polymer complex of a basic polymer and an acidic polymer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

To describe in detail about the present invention, the recording medium of the present invention is characterized principally in that its ink receiving layer comprises a polymer complex of a basic polymer and an acidic polymer and the objects of the present invention can be accomplished primarily by such a characteristic.

The recording medium of the present invention generally comprises a substrate as the supporting material and a recording surface, namely an ink receiving layer, provided on its surface. For example, particularly preferred embodiments may include the following:

(1) the embodiment in which both of the substrate and the ink receiving layer are light transmissive, and the recording medium as a whole is light transmissive; and

(2) the embodiment in which the surface of the ink receiving layer is smooth and glossy.

In each embodiment, the ink receiving layer may also serve as a support.

The present invention is described in more detail by referring to some preferred embodiments as mentioned above as typical examples.

The polymer complex which characterizes principally the present invention comprises a basic polymer and an acidic polymer.

In the prior art, polymer complexes comprising a basic polymer and an acidic polymer are known as disclosed in, for example, Japanese Patent Publication Nos. 37017/1976 and 42744/1980.

In the present invention, preferable basic polymers may include, for example, those as set forth below:

Homopolymers or random copolymers, block copolymers or graft copolymers with other monomers in general of N-vinyl-lactams such as N-vinylpyrrolidone, N-vinyl-3-methylpyrrolidone, N-vinyl-5-methylpyrrolidone, N-vinyl-3,3,5-trimethylpyrrolidone, N-vinyl-3-benzylpyrrolidone, N-vinylpiperidone, N-vinyl-4-methylpiperidone, N-vinylcaprolactam, N-vinylcaprylactam, N-vinyl-3-morpholine, N-vinyl-thiopyrrolidone, N-vinyl-2-pyrrolidone and the like;

Homopolymers or random copolymers, block copolymers or graft copolymers with other monomers in general of N-vinyl cyclic carbamates such as N-vinyl-2-oxazolidone, N-vinyl-5-methyl-2-oxazolidone, N-vinyl-5-ethyl-2-oxazolidone, N-vinyl-4-methyl-2-oxazolidone, N-vinyl-2-thiooxazolidone, N-vinyl-2-mercapto-benzothiazole and the like;

Homopolymers or random copolymers, block copolymers or graft copolymers with other monomers in general of N-vinylimidazoles such as N-vinylimidazole, N-vinyl-2-methylimidazole, N-vinyl-4-methylimidazole and the like;

Homopolymers or random copolymers, block copolymers or graft copolymers with other monomers in general of 2- or 4-vinyl-pyridine; etc.

Other copolymerizable monomers to be used for the above copolymers may include methacrylate, acrylate, acrylamide, acrylonitrile, vinyl ether, vinyl acetate, vinylimidazole, ethylene, styrene and other monomers in general. Particularly useful in the present invention are homopolymers and copolymers of N-vinylpyrrolidone, N-vinylpiperidone, N-vinylcaprolactam, N-vinylmorpholine, N-vinyl-2-oxazolidone, N-vinyl-5-methyl-2-oxazolidone, etc. The nitrogen-containing monomer as described above in the copolymers is preferably contained in an amount of 50 mole % or more.

On the other hand, the acidic polymer capable of forming a polymer complex with the above basic polymer may include, for example, polymers shown below. The "acidic polymer" in the present invention is also inclusive of those having alcoholic hydroxyl groups, other than those having sulfonic acid groups, carboxylic acid groups, sulfuric acid ester groups, phosphoric acid ester groups, or phenolic hydroxyl groups in its molecule.

1. Polymers having carboxylic acid groups:

Carboxyl terminated polyesters obtained by the reaction of polycarboxylic acids such as citric acid, tartaric acid, phthalic acid with polyhydric alcohols such as ethylene glycol, 1,4-butane diol, diethylene glycol, etc. in the presence of acids in excess.

Acidic cellulose derivatives modified with various kinds of polycarboxylic acids (see Japanese Patent Publication No. 5093/1960);

Homopolymers or random copolymers, block copolymers or graft copolymers with other monomers in general of vinyl ether ester monomers of polycarboxylic acids, etc. (see Japanese Patent Publication No. 8495/1960);

Homopolymers or random copolymers, block copolymers or graft copolymers with other monomers in general of vinyl ether ester monomers of acrylic acid, methacrylic acid, etc.;

Homopolymers or random copolymers, block copolymers or graft copolymers with other monomers in general of α, β-unsaturated vinyl monomers such as maleic anhydride, itaconic acid, etc (see Gosei Kobunshi (Synthetic Polymer) (III), edited by Murahashi, Inoue, Tani, p.250-257 and p.374-380, published by Asakura Shoten, 1971);

2. Polymers having sulfonic acid groups:

Cellulose derivatives such as O-ethylcellulose acetate hydrogen sulfate hydrogen phthalate, cellulose acetate hydrogen sulfate hydrogen phthalate, ethylcellulose hydrogen-O-sulfobenzoate, O-P-sulfonbenzylcellulose acetate, O-ethyl-O-P-sulfoethylcellulose acetate, etc. (see Japanese Patent Publication No. 5093/1960);

Sulfonic acid-modified polymers of polyvinyl alcohol or vinyl alcohol copolymer with sulfonic acid compounds (e.g. O-sulfobenzoic acid, sulfopropionic acid, sulfovaleric acid, sulfobenzaldehyde, sulfophthalic acid, etc.);

3. Polymers having hydroxyl group:

Ethylcellulose, benzylcellulose, hydroxyethylcellulose, hydroxyethyl/ethylcellulose, hydroxyethyl/benzylcellulose, etc.;

Other homopolymers, random copolymers, block copolymers or graft copolymers with other monomers in general with other monomers having sulfonic acids or phenol groups;

Various acidic modified polymers with other compounds containing carboxylic groups, sulfonic acid groups or phenol groups.

As the phenolic acidic polymers, there may be included specifically those having phenolic hydroxyl groups in their main chains and/or side chains.

Such phenolic acidic polymers may include so-called phenol resins or initial condensates thereof obtained by addition-condensation reaction of monomers of phenols having hydroxyl groups in the aromatic ring such as phenol, m-cresol, 3,5-xylenol, p-alkylphenol, resorcin, α- or β-naphthol, etc. or derivatives thereof with an aldehyde such as formalin. These polymers may be either homopolymers or copolymers, which may be either random, block or graft copolymers.

Such phenolic acidic polymers may have various molecular weights from relatively lower molecular weights which are soluble in water or organic solvents to those with higher molecular weights which are insoluble and unmeltable. In the present invention, those soluble in water, organic solvents such as alcohol, ketone, etc., for example, initial condensates of phenol resins are particularly useful.

These phenolic acidic polymers are generally hydrophilic, but they are hard and can form only brittle coated films, and therefore are not applicable at all for the ink receiving layer of a recording medium. However, through formation of a complex with a basic polymer as described above, ink receiving layers having various excellent performances can be formed.

As the polymer having phenolic hydroxyl groups in the side chain, there may be included polymers or copolymers with other monomers in general of vinyl monomers having phenolic hydroxyl groups such as vinylphenol, vinylnaphthol, etc.; further modified polymers of polymers in general having functional groups such as hydroxyl groups, carboxyl groups, amino groups, etc. modified with compounds having phenolic hydroxyl groups, which can be used similarly as the phenol resins as described above.

Any of the acidic polymers as described above can preferably be used:

The present inventors have investigated comprehensively the mixtures of the basic polymers and acidic polymers as described above, and found that mixing of these polymers in a solution gives a polymer complex different from either starting polymer through some interaction between both polymers, and mixing of both polymers in a relatively poor solvent results in precipitation of the polymer complex, while mixing in a relatively good solvent results in marked increase of the viscosity, thus giving a mixture having properties different from those of a simple mixture of both polymers employed.

Accordingly, the term "polymer complex" to be used in the present invention means a polymer complex comprising polymers as described above (as to details about basic polymers, acidic polymers and polymer complexes comprising these polymers, see Japanese Patent Publication No. 37017/1976 and Japanese Patent Publication No. 42744/1980).

The present inventors have further investigated comprehensively uses of these polymer complexes, and found that these polymer complexes, although they are markedly hydrophilic, are resistant to water and humidity and exhibit ink receptivity comparable to that of water-soluble polymers of the prior art to give sharp images, and yet their surfaces will not become sticky even under highly humid conditions. Further, it has also been found that, when a phenolic polymer is used as the acidic polymer, the strength at the portion which has received ink becomes more strong, and the film will not easily be peeled off nor broken even when touched with a finger or a thing.

Because of general insolubility of the above-mentioned polymer complexes in a relatively poor solvent such as water, alcohols, esters, and hydrocarbons, the polymer complex of the present invention may be isolated by dissolving each of the starting polymers in a poor solvent respectively and then mixing both solutions. On the other hand, a solution of a polymer complex can be obtained by dissolving the starting polymers in a relatively good solvent such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, etc.

Preferable basic polymers and acidic polymers for formation of a polymer complex as described above may be those having respective molecular weights of 500 or more, preferably 1,000 or more, and an ink receiving layer with great strength excellent in ink receptivity giving sharpness of the image, water resistance and ink resistance can be formed from both types of polymers of such molecular weights.

The proportion of both polymers to be employed may be within the range of 20/1 to 1/10 in terms of weight ratio of basic polymer to acidic polymer, preferably a ratio at which the basicity and the acidity of the respective polymers are approximately equal. Outside the range of the above weight ratio, bonding between both polymers will be insufficient, whereby the objects of the present invention cannot fully be achieved. For example, With a large excess of the basic polymer, water resistance will be reduced, while with a large excess of the acidic polymer, ink receptivity will be reduced.

As disclosed in Japanese Laid-open Patent Publication No. 174382/1984, for further improvement of ink fixing characteristic and stickiness on the surface at the printed portion, a condensation product of D-sorbitol and benzaldehyde may be added to the above polymer complex at a proportion of 0.1 to 50 % by weight.

The ink receiving layer of the recording medium of the present invention can be formed by use of the polymer complex as described above, but it is also possible in the present invention to use additionally other polymers than the polymer complex as described above, for example, other light transmissive polymers in combination with the above polymer complex.

Preferred as such other polymers are natural resins such as albumin, gelatin, casein, starch, cationic starch, gum arabic, sodium alginate, etc.; and synthetic resins such as polyvinyl alcohol, polyamide, polyacrylamide, quaternarized polyvinyl pyrrolidone, polyethyleneimine, polyvinylpyridinium halide, melamine resin, polyurethane, polyester, sodium polyacrylate, etc. At least one of these materials may be used in combination, if desired.

Further, for reinforcement of the ink receiving layer and/or improvement of adhesion of the layer to substrate, resins such as SBR latex, NBR latex, polyvinylformal, polymethyl methacrylate, polyvinylbutyral, polyacrylonitrile, polyvinyl chloride, polyvinyl acetate, phenol resin, alkyd resin may also be used in combination, if necessary.

For improvement of ink absorptivity of the ink receiving layer, it is possible to disperse filers such as silica, clay, talc, diatomaceous earth, calcium carbonate, calcium sulfate, barium sulfate, aluminum silicate, synthetic zeolite, alumina, zinc oxide, lithopon, satin white, etc. in the ink receiving layer.

As for the substrate to be used as the supporting material for the ink receiving layer in the present invention, it may be any substrate known in the art, transparent or opaque. Preferable examples of transparent substrates may include films or plates such as of polyester resins, diacetate resins, polycarbonate resins, polyvinyl chloride resins, polyimide resins, cellophane, celluloid, etc. and glass plates. Preferable opaque substrates may include, for example, paper, cloth, wood, metal plate, synthetic paper in general, or otherwise the above transparent substrates which have been made opaque according to known means.

The recording medium of the present invention is formed by use of the main materials as described above. In the preferable embodiment (1) as mentioned above, both of the substrate and the ink receiving layer are light transmissive, with the linear transmittance being 10 % or higher, and it is an embodiment in which the recording medium as a whole is light transmissive.

The recording medium of this embodiment is particularly excellent in light transmissivity and employed primarily in the uses such as an OHP, etc. in which recorded image is projected onto a screen, etc. by means of an optical instrument, thus being useful for observation with transmitted light.

Such a light transmissive recording medium can be prepared by forming a light transmissive ink receiving layer from a polymer complex as described above alone or a mixture of this polymer complex with another light transmissive polymer on the light transmissive substrate as described above.

As the method for forming such an ink receiving layer, there may preferably be employed a method in which a coating solution is prepared by dissolving or dispersing the above polymer complex or a mixture with another appropriate polymer and said solution is coated on the light transmissive substrate according to the known method such as roll coating, rod bar coating, spray coating, air knife coating, etc., followed by rapid drying, or a method in which one solution of either the basic polymer or the acidic polymer is applied and then the other solution to form a polymer complex on the substrate. It is also possible to use the method in which the above polymer complex alone or a mixture together with another polymer is subjected to hot melt coating or the method in which a single sheet for ink receiving layer is once formed from the material as described above, and said sheet is laminated on the above substrate.

The recording medium according to the embodiment (1) formed as described above is a light transmissive recording medium having sufficient light transmissivity.

The sufficient light transmissivity as herein mentioned means that the linear transmittance of the recording medium should desirably exhibit at least 2 %, preferably 10 % or higher.

If the linear transmittance is 2 % or higher, the recorded image can be observed by projection by, for example, an OHP onto a screen. Further, in order for the fine portion of the recorded image to be observed sharply, the linear transmittance should desirably be 10 % or higher.

The linear transmittance T (%) as herein mentioned is a value which is determined by measuring the spectral transmittance of the linear light which enters a sample perpendicularly, transmits through the sample, passes through a slit on the light receiving side which is located at least 8 cm apart form the sample on the line extended from the incident light pathway and is received on a detector, by means of, for example, 323 Model Hitach Automatic Recording Spectrophotometer (produced by Hitachi, Ltd.), further determining the Y value of tristimulus values of color and calculating from the following formula:

$$T = Y/Yo \times 100 \quad (1)$$

T: Linear transmittance

Y: Y value of sample

Yo: Y value of blank

Thus, the linear transmittance as mentioned in the present invention is relative to linear light, and it is different from diffuse transmittance (transmittance is determined so as to be inclusive of diffused light by providing an integrating sphere at the back of a sample) or opacity (determined from the ratio of values when white and black backings are placed on the back of a sample) according to the method in which light transmissivity is evaluated with diffused light.

Since what becomes as problem in an instrument utilizing optical techniques is the behavior of linear light, it is particularly important to determine the linear transmittance of a recording medium in evaluation of the light transmissivity of the recording medium to be used in such an instrument.

For example, in the case of observing a projected image by OHP, in order to obtain an image with high contrast between the recorded portion and the non-recorded portion, sharp and easy to see, the non-recorded portion in the projected image is required to be light, namely the linear transmittance of the recording medium should be at a certain level or higher. In the test using a test chart in an OHP, for obtaining an image suited for the above purpose, the linear transmittance of the recording medium needs to

be 2 % or higher, preferably 10 % or higher in order to obtain a sharper image. Therefore, the recording medium suited for this purpose is required to have a linear transmittance which is at least 2 %.

The embodiment (2) as mentioned above is also a modification of the above embodiment (1), and it is characterized by that the surface of its ink receiving layer is smooth and has a 45 degree mirror surface gloss of at least 30 % based on JIS Z8741.

The recording medium of said type is particularly excellent in surface gloss and particularly useful as a recording medium for observation of a surface image which is of full color and excellent in sharpness. The recording medium according to this embodiment may be either transparent or opaque, and any of the above transparent and opaque materials can be used. Also, the ink receiving layer may be either transparent or opaque. The materials and the method to be used for formation of the ink receivng layer may be the same as described above embodiment (1), but the above-mentioned filers can be used even to the extent such that the ink receiving layer may become opaque, provided that the surface of the ink receiving layer can retain its smoothness.

Further, if desired, in addition to the coating methods as described above, it is also possible to employ the cast coating method or to effect glossing by means of calender rolls.

In the present invention as described above, the ink receiving layer to be formed on the substrate may have a thickness of generally 1 to 200 μm, preferably 3 to 100 μm, more preferably 5 to 30 μm.

Further, in the present invention, organic or inorganic fine powder imparted at a proportion of about 0.01 to about 1.0 g/m² on the recording surface of the recording medium of various embodiments as described above will further improve the conveying characteristic within the printer, antiblocking characteristic during piling, fingerprint resistance, etc. of the recording medium obtained.

Having described above by referring to examples of typical embodiments of the recording medium of the present invention, the recording medium of the present invention will not of course be limited to these embodiments. In either of these embodiments, the ink receiving layer and/or the ink permeable layer may contain various known additives, including dispersing agents, fluorescent dyes, pH controllers, defoaming agents, lubricants, preservatives, surfactants, etc.

The recording medium of the present invention is not necessarily required to be colorless, but it may also be a colored recording medium.

The recording medium of the present invention can exhibit excellent ink receptivity similarly as that having an ink receiving layer formed with a water-soluble polymer of the prior art and provide a recorded image of excellent sharpness, with its surface not becomig tacky or sticky.

Thus, even when inks with different colors may be attached on the same spot to overlap each other within a short time, there is no such phenomenon as flowing-out or oozing-out, whereby the ink receiving layer will not reduce its strength and a sharp image can be obtained with high resolution.

Moreover, since the recording medium of the present invention does not become tacky or sticky on the surface of the ink receiving layer, being different from the recording medium using a water-soluble polymer of the prior art, even when recording as described above may be performed under highly humid conditions, there will be caused no trouble in the printer: neither blocking nor color transfer occurs when they are placed one upon another.

Such excellent effects under highly humid conditions may be considered to be due to formation of a polymer complex through generation of some weak bonding between the molecules of the two kinds of the polymers used for formation of the ink receiving layer such as electrostatic force between ions, hydrogen bonding, Van der Waals force, partial charge transfer, etc., thus exhibiting excellent water resistance even under highly humid conditions, while retaining high ink receptivity.

It has been entirely unexpected that such excellent effects as described above can be accomplished by a water-insoluble polymer complex. This may be considered to be due to the fact that the ink consisting of a water-polyhydric alcohol mixture system will promote reception of ink imparted by temporarily dissolving or swelling the ink receiving layer of the recording medium without lowering its film strength and, after reception, the ink receiving layer will be returned to the original water-insoluble polymer complex through absorption and evaporation of moisture. Such a theory is a mere speculation and will be in no way restrictive of the present invention.

In the present invention, it is also possible to provide a recording medium excellent in surface gloss which has not been found in the recording medium for ink jet recording of the prior art. Further, it can be applied for uses other than surface image observation of the prior art such as for observation by projection of a recorded image by an optical instrument such as a slide, an OHP, etc., a color resolution plate during preparation of a positive plate for color printing, or a CMF, etc. to be used for color display such as liquid crystal, etc.

The present invention is described in more detail by referring to the following Examples, in which parts are based on weight.

Example 1

An amount of 66 parts of an aqueous 10 % polyvinylpyrrolidone solution (PVPK-90, produced by GAF) was mixed with 34 parts of an aqueous 10 % solution of a methyl vinyl ether/maleic anhydride copolymer (GANTREZ AN-169, produced by GAF). The mixture gelled to form a polymer complex. On heating the complex to 90 °C with addition of N,N-dimethylformamide, it was solubilized into a solution, which was used as the coating solution.

As a light transmissive substrate, a polyethylene terephthalate film with a thickness of 100 μm (produced by Toray) was employed, and a coating solution having the composition shown above was applied onto this substrate film to a thickness after drying of 8 μm according to the bar coater method, and dried under the conditions of 80 °C and 10 minutes to give a light transmissive recording medium of the present invention.

The recording medium of the present invention thus obtained was found to be colorless and transparent.

Examples 2 - 8

By use of the compositions as shown below, coating solutions were prepared and 4 kinds of light transmissive recording media of the present invention and 3 kinds of comparison recording media were obtained by forming an ink absorbing layer on the same polyethylene terephthalate film as used in Example 1 in the same manner as in Example 1.

Example 2

Polyvinyl-pyrrolidone (PVPK-90, produced by GAF)

(10 % aqueous solution) 66 Parts

Methyl vinyl ether/maleic anhydride mono-ethyl ester copolymer (GANTREZ ES 425, produced by GAF)

(diluted to 10 % ethanol solution) 34 Parts

Example 3

Polyvinyl-pyrrolidone (PVPK-90, produced by GAF)

(10 % aqueous solution) 75 parts

Isobutylene/maleic anhydride copolymer (ISOBAM 10, produced by Kuraray Isoprene)

(10 % DMF solution) 25 parts

Example 4

Polyvinyl-pyrrolidone (PVPK-90, produced by GAF)

(10 % aqueous solution) 66 Parts

Tannic acid (10 % aqueous solution) 34 Parts

Example 5

Polyvinyl-pyrrolidone/vinyl acetate copolymer
(LUVISCOL 73E, produced by Yuka-Badische)
(diluted to 5 % ethanol solution) 50 Parts

Hydroxyethyl-cellulose
(HEC AG-15, produced by Fuji Chemical)
(5 % ethanol solution) 50 Parts

Example 6

Poly-N-vinylimidazole
(10 % ethanol solution) 66 Parts

Methyl vinyl ether/monoethyl maleate
(10 % ethanol solution) 34 Parts

Example 7

Poly-N-vinyl-5-methyl-2-oxazolidone
(5 % ethanol solution) 50 Parts

Hydroxyethyl-cellulose
(5 % aqueous solution) 50 Parts

Example 8

Polyvinyl-pyrrolidone
(10 % aqueous solution) 56 Parts

Methyl vinyl ether/monoethyl maleate
(10 % ethanol solution) 19 Parts

D-sorbitol/benzaldehyde condensate
(GELOL D, produced by Shinnippon Rika)
(10 % DMF solution) 25 Parts

Example 9

An amount of 88 parts of 10 % solution of a polyvinyl-pyrrolidone (PVPK-90, produced by GAF) in dimethylformamide (hereinafter referred to as DMF) was mixed with 12 parts of a 10 % DMF solution of a novolac type phenol resin (RESITOP PSK-2320, produced by Gun-ei Kagaku). The mixture gelled to form a polymer complex. On heating the complex to 90 °C with stirring solubilized it into a solution, which was used as the coating solution.

As a light transmissive substrate, a polyethylene terephthalate film with a thickness of 100 µm (produced by Toray) was employed, and a coating solution having the composition shown above was applied onto this substrate film to a thickness after drying of 8 µm according to the bar coater method, and dried under the conditions of 80 °C and 10 minutes to give a light transmissive recording medium of the present invention.

The recording medium of the present invention thus obtained was found to be colorless and transparent.

Examples 10 - 12 and Comparative examples 1 - 2

By use of the compositions as shown below, coating solutions were prepared and 3 kinds of light transmissive recording media of the present invention and 2 kinds of recording media for comparative purpose were obtained by forming an ink absorbing layer on the same polyethylene terephthalate film as used in Example 9 in the same manner as in Example 9.

Example 10

Vinyl-pyrrolidone/dimethylaminoethyl methacrylate copolymer (COPOLYMER 845, produced by GAF) (10 % ethanol/DMF solution)	70 Parts
Novolac type phenol resin (RESITOP RSF-4261) (10 % DMF solution)	30 Parts

Example 11

Polyvinyl-pyrrolidone (PVPK-90, produced by GAF) (10 % DMF solution)	87 Parts
Resol type phenol resin (RESITOP PS-2211) (10 % ethanol/DMF solution)	13 Parts

Example 12

Polyvinyl-pyrrolidone (PVPK-90, produced by GAF) (10 % DMF solution)	85 Parts
Novolac type phenol resin (RESITOP K-2320) (10 % ethanol/DMF solution)	10 Parts
D-sorbitol/benzaldehyde condensate (GELOL D, produced by Shinnippon Rika) (10 % DMF solution)	5 Parts

Comparative example 1

Polyvinyl-pyrrolidone (PVPK-90, produced by GAF)	10 Parts
DMF	90 Parts

Comparative example 2

Polyvinyl-pyrrolidone (PVPK-90, produced by GAF) (10 % DMF SOLUTION)	50 Parts
Polyvinyl alcohol (PVA-217, produced by Kuraray) (10 % aqueous solution)	50 Parts

On the recording media of the above Examples and Comparative Examples, ink jet recording was practiced by use of the four kinds of ink as shown below by means of a recording device having an on-demand type ink jet recording head which discharges ink by a piezoelectric vibrator (discharge orifice diameter: 60 μm, piezoelectric vibrator driving voltage: 70 V, frequency 2 KHz).

Yellow ink (composition)

C.I. Direct Yellow 86	2 Parts
Diethylene glycol	25 Parts
Polyethylene glycol #200	15 Parts
Water	60 Parts

Red ink (composition)

C.I. Acid Red 35	2 Parts

Diethylene glycol	25 Parts
Polyethylene glycol #200	15 Parts
Water	60 Parts

Blue ink (composition)

C.I. Direct Blue 86	2 parts
Diethylene glycol	25 Parts
Polyethylene glycol #200	15 Parts
Water	60 Parts

Black ink (composition)

C.I. Food Black 2	2 Parts
Diethylene glycol	25 Parts
Polyethylene glycol #200	15 Parts
Water	60 Parts

The results of evaluation of the recording media of Examples 1 - 8 are shown in Table 1.

The respective evaluation items in Table 1 were measured following the methods as described below.

(1) Ink fixing time was determined by leaving the recording medium after recording to stand at room temperature and measuring the time for ink drying to such a degree that the ink does not stick a touched finger.

(2) Dot density was measured for black dots by means of Sakura Microdensitometer PDM-5 (produced by Konishiroku Photo Industry K.K.) by applying JIS K7505 for printed microdots.

(3) OHP adaptability was evaluated as a typical example of an optical instrument. The recorded image was projected by OHP onto a screen, and judged by visual observation. One which can provide a projected image which is light at non-recorded portion, high in OD (optical density) of recorded image, sharp and easy to see with high contrast was rated as ○; one which can provide a projected image which is slightly dark at non-recorded portion, slightly low in OD of recorded image and not clearly discriminable between the lines with a pitch width of 0.5 mm and a boldness of 0.25 mm was rated as △; one which can provide a projected image which is considerably dark at non-recorded portion, considerably low in recorded image and not clearly discriminable between the lines with a pitch width of 1 mm and a boldness of 0.3 mm, or which is indiscriminable between non-recorded portion and recorded image, was rated as x.

(4) Linear transmittance was determined by measuring the spectral transmittance by means of 323 Model Hitach Automatic Recording Spectrophotometer (produced by Hitachi, Ltd.) while maintaining the distance from the sample to the window on the light receiving side at about 9 cm and calculating from the formula (1) mentioned above.

(5) Conveying performance was rated as x, when the recording medium could not be conveyed with the delivery roller of the printer due to stickiness on the ink receiving layer surface when it was mounted on the printer under the conditions of 35 °C and 85 % RH, or otherwise as ○.

(6) Blocking was evaluated by placing a pure paper in close contact on the printed surface one hour after printing, followed by storage for 12 hours, and rated as ○ when no

adhesion occurred between the recording medium and the pure paper, or otherwise as x. If no adhesion occurred even when the same test was conducted 10 minutes after printing, it was rated as ◎.

(7) Formation of polymer complex was evaluated by the presence of abrupt increase of viscosity or formation of gel when the respective solutions of a basic polymer and a phenolic acidic polymer were mixed together as being ○, or otherwise as x.

The results of evaluation of the recording media of Examples 9 - 12 and Comparative examples 1 - 2 are shown in Table 2.

Measurements of evaluation items in Table 2 were also conducted for the item (8) in addition to the above items - (1) - (7).

(8) Film strength was evaluated by rubbing the surface of the solid printed portion of the ink receiving layer with a finger 5 minutes after printing, and rated as x when the coating lacked strength and is peeled off from the base film or broken at the image, or otherwise as ○.

Table 1

	Example							
	1	2	3	4	5	6	7	8
Ink fixing time	10 min.	5 min.	3 min.	10 min.	3 min.	5 min.	5 min.	2 min.
Dot density	1.1	1.1	1.1	1.2	1.0	1.1	1.0	1.1
OHP adaptability	○	○	○	○	○	○	○	○
Linear transmittance	74%	79%	79%	78%	74%	78%	78%	76%
Conveying performance	○	○	○	○	○	○	○	○
Blocking	○	○	○	○	○	○	○	○
Formation of polymer complex	○	○	○	○	○	○	○	○

Table 2

	Example			
	1	2	3	4
Ink fixing time	3 min.	5 min.	3 min.	2 min.
Dot density	1.1	1.1	1.1	1.1
OHP adaptability	○	○	○	○
Linear transmittance	79%	79%	79%	74%
Conveying performance	○	○	○	○
Blocking	○	○	○	◎
Film strength	○	○	○	○
Formation of polymer complex	○	○	○	○

	Comparative Example	
	1	2
Ink fixing time	10 min.	1 min.
Dot density	1.2	1.1
OHP adaptability	○	○
Linear transmittance	80%	80%
Conveying performance	x	x
Blocking	x	x
Film strength	x	x
Formation of polymer complex	-	x

Claims

1. A recording medium, which comprises having an ink receiving layer containing a polymer complex of a basic polymer and an acidic polymer.

2. A recording medium according to claim 1, wherein said basis polymer is a polymer of at least one compound selected from N-vinyllactams, N-vinyl cyclic carbamates, N-vinylimidazoles, and 2- or 4- vinylpyridine.

3. A recording medium according to claim 1 or claim 2 wherein said acidic polymer is a polymer having any one of a carboxylic acid group, a sulfonic acid group and a hydroxyl group in the molecule.

4. A recording medium according to any preceding claim wherein the mixing ratio of said basic polymer and said acidic polymer is within the range of from 20:1 to 1:10.

5. A recording medium according to any preceding claim wherein said ink receiving layer has a thickness from 1 to 200 μm.

6. A recording medium according to any preceding claim wherein said ink receiving layer is provided on a substrate.

7. A recording medium according to claim 6, wherein said substrate is selected from films of polyester resin, diacetate resin, triacetate resin, acrylic resin, polycarbonate resin, polyvinyl chloride resin, cellophane, celluloid and polyimide resin, and glass plates.

8. A recording medium according to any preceding claim wherein said ink receiving layer is light transmissive.

9. A recording medium according to any preceding claim wherein said substrate is light transmissive.

10. A recording method in which recording is performed by forming liquid droplets of a recording liquid and permitting the liquid droplets to attach on the surface of a recording medium, wherein the recording liquid is an aqueous ink and the surface of the recording medium contains a polymer complex of a basic polymer and an acidic polymer.

11. A method according to claim 10 in which there is used a recording medium according to any of claims 1 to 9.